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Effect of the molar SO_3/LAB ratio on free-oil amount and composition during LAB sulphonation

Free-oil amount and composition of an LAB-sulphonic acid were determined before and after hydrolysis as a function of the SO_3/LAB molar ratio. HPLC analysis indicates that the free-oil before hydrolysis is composed of anhydrides, LAB and sulphones and that the amount and composition strongly change as the SO_3/LAB molar ratio increases. Additionally the distribution of anhydride, LAB and sulphone homologues were determined by HPLC and compared with the starting LAB. By this method the kinetics of the different reactions could be established.

Der Freiölgehalt und die Zusammensetzung einer LAB-Sulfonsäure wurden als Funktion des SO_3/LAB -Molverhältnisses vor und nach der Hydrolyse bestimmt. Die HPLC-Analyse zeigt, daß sich das Freiöl vor der Hydrolyse aus Anhydriden, LAB und Sulfonen zusammensetzt, und daß sich seine Menge und Zusammensetzung stark mit steigendem SO_3/LAB -Molverhältnis ändern. Darüber hinaus wurde die Verteilung der Anhydrid-, LAB- und Sulfonhomologen bestimmt und mit der Homologenverteilung im Ausgangsprodukt verglichen. Auf diese Weise konnte die Kinetik der verschiedenen Reaktionen erhalten werden.

1 Introduction

In a previous study [1] we described a method for the analysis and characterization of free-oil amount and composition of a sulphonic acid derived from a commercial linear alkylbenzene (LAB) prior to hydrolysis. Linear alkylbenzene sulphonation consists of three steps, reaction, digestion and hydrolysis. In the a.m. paper the free-oil was extracted after digestion (before hydrolysis) and anhydrides were esterified by reaction with ethanol. The HPLC-analysis of the free-oil indicated that its compounds were esterified anhydrides (esters), LAB and sulphones. After hydrolysis the anhydrides were completely hydrolyzed, only LAB and sulphones remained as free-oil compounds.

According to the description in [1] the material balance was carried out in two steps, namely:

- Anhydrides were determined gravimetrically as ethyl esters by difference between free-oil before and after hydrolysis
- LAB and sulphones were determined by quantitative HPLC-analysis of free-oil after hydrolysis.

Based on this method, it was found worthwhile to pursue the evolution of these minor by-products of an LAB sulphonated at different SO_3/LAB molar ratios before and after hydrolysis.

2 Results and discussion

The starting LAB was a commercial product from Petresa with the following composition: phenyl C_{10} 10.8; phenyl C_{11} 39.7; phenyl C_{12} 31.5; phenyl C_{13} 17.8%.

The sulphonations were carried out in a laboratory pilot plant under the following conditions: Temperature 45°C; SO_3/N_2 4.34 wt%; SO_3/LAB molar ratios: 1, 1.02, 1.05, 1.07 and 1.1.

Free-oil extraction procedures and HPLC-analysis methods are given in detail in [1].

2.1 Free-oil amount before and after hydrolysis

The experimental results are given in Table 1 and plotted in Fig. 1. They indicate that the free-oil amount in sulphonic

Table 1. Free-oil amount before and after hydrolysis (wt.% in sulphonic acid)

SO_3/LAB	1.0	1.02	1.05	1.07	1.1
F.o. before	7.6	6	5.4	5.3	5.05
F.o. after	5	3.5	2.3	1.5	0.9

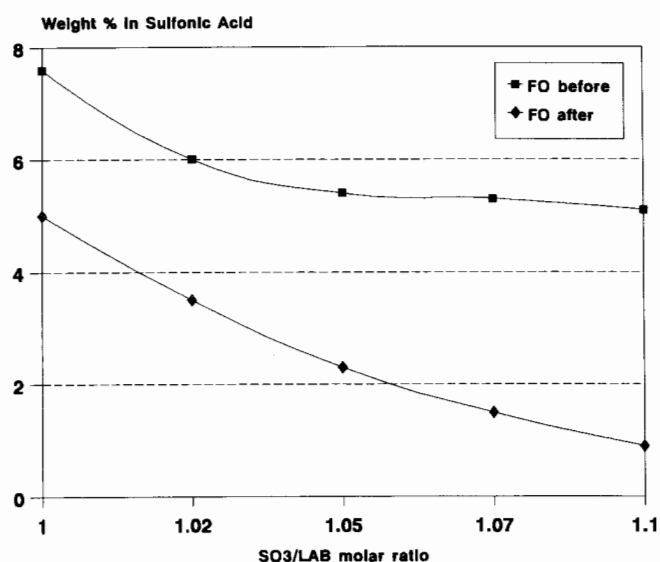


Fig. 1. Free-oil amount vs. SO_3/LAB molar ratio before and after hydrolysis

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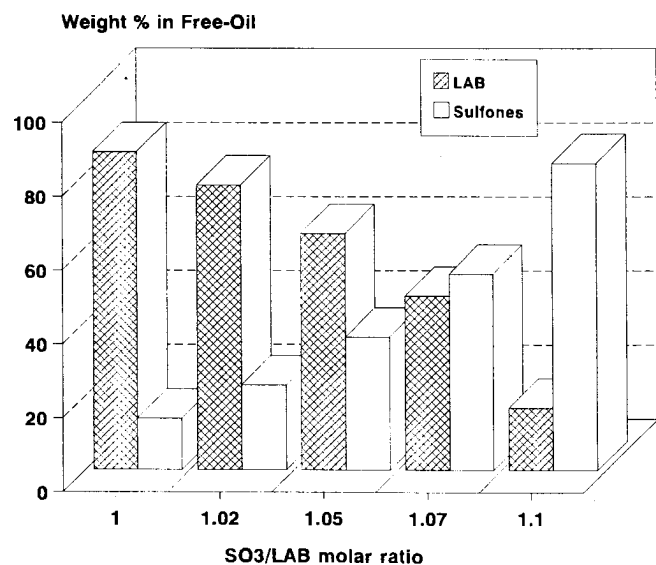


Fig. 5. Free-oil composition after hydrolysis (wt% in free-oil)

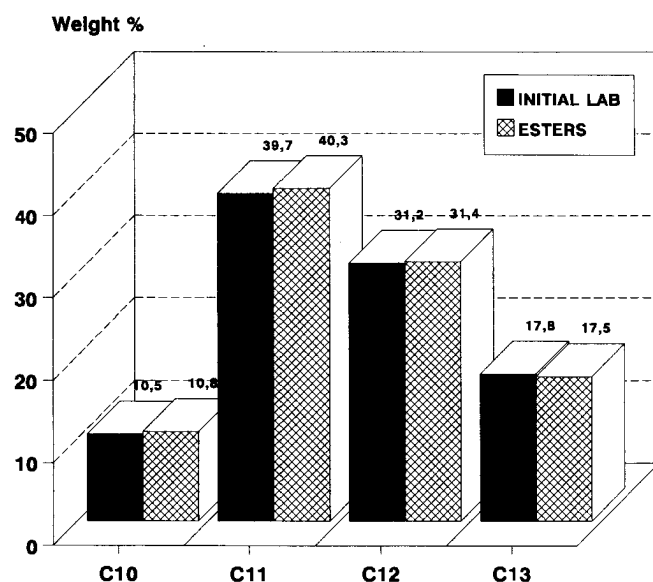


Fig. 6. Anhydrides distribution

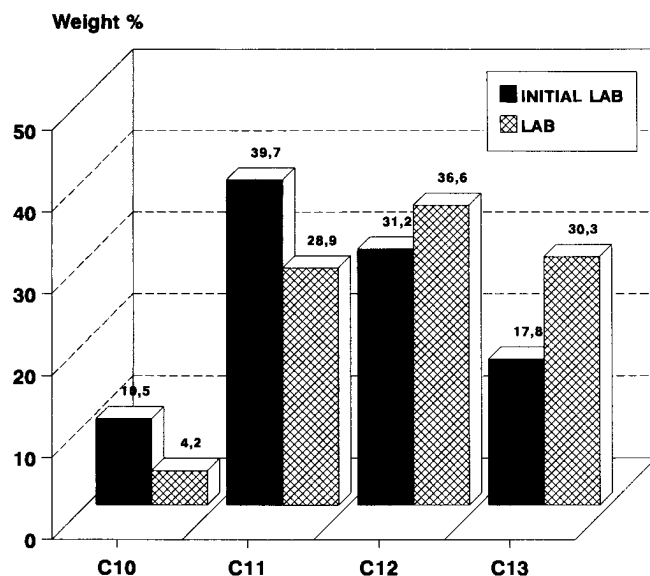


Fig. 7. LAB distribution

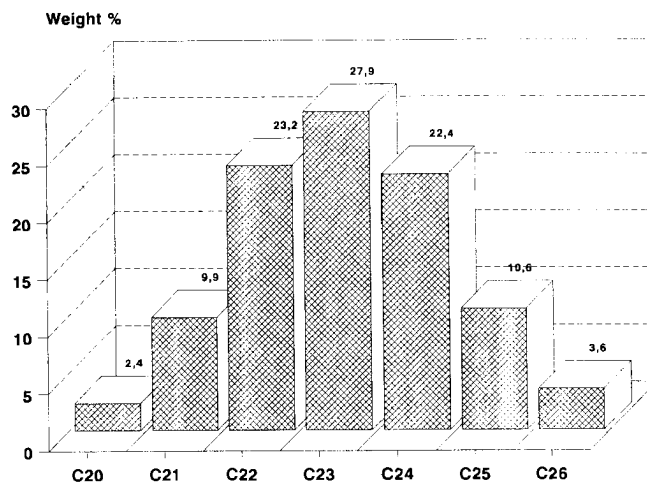


Fig. 8. Sulfoxes distribution

changes because LAB decreases as the SO₃/LAB molar ratio increases (Fig. 5).

A first conclusion can be drawn: Free-oil amount and composition change considerably with increasing SO₃ to LAB molar ratio.

2.3 Distributions of anhydrides, non-sulphonated LAB and sulfoxes

The distributions of each compound were calculated based on HPLC analysis. The results are independent of the SO₃/LAB molar ratio.

Anhydrides

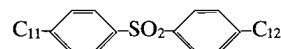
Anhydrides distribution calculated as esters is given in Fig. 6, together with the initial or starting LAB distribution. The fact that both distributions are identical indicates that the kinetic of anhydride formation is independent of the alkyl chain length.

LAB

In agreement with the literature [2, 3], the composition of non-sulphonated LAB shows that the reaction rate of LAB with SO₃ to produce sulphonic acid decreases as the alkyl chain length increases. The results are given in Fig. 7.

Sulfoxes

The distribution of sulfoxes is shown in Fig. 8. Taking into account that a sulphone consists of two LAB homologues separated by an SO₂ group, a C₂₃ sulphone could result from the combination of a C₁₀-LAB with a C₁₃ one or, more likely, from the combination of a C₁₁-LAB with a C₁₂ one.



According to the analytical results, it is evident that the distribution of sulfoxes corresponds to the starting LAB distribution, i.e. the most abundant sulfoxes correspond to the most abundant LAB homologues C₁₁ and C₁₂, as the possibilities of reaction strongly depend on the initial reactants concentrations.

Acknowledgement

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Table 2. Free-oil composition before hydrolysis (wt.% in sulphonic acid)

SO ₃ /LAB	1.0	1.02	1.05	1.07	1.1
Esters	2.6	2.5	3.1	3.8	4.2
LAB	4.3	2.7	1.5	0.7	0.15
Sulphones	0.7	0.8	0.8	0.8	0.7
Total	7.6	6	5.4	5.3	5.05

Table 3. Free-oil composition before hydrolysis (wt% in free-oil)

SO ₃ /LAB	1.0	1.02	1.05	1.07	1.1
Esters	34	42	59	72	82
LAB	57	45	28	13	3
Sulphones	9	13	13	15	15
Total	100	100	100	100	100

acid decreases as the SO₃/LAB molar ratio increases within the experimental range. The different slopes of both curves prior and after hydrolysis will be interpreted based on free-oil composition as will be seen later.

2.2 Free-oil composition before and after hydrolysis

Before hydrolysis

Distributions of esterified anhydrides (esters), LAB and sulphones, expressed as weight percent in sulphonic acid and weight percent in free-oil, respectively, are given in Tables 2 and 3 and are plotted in Figs. 2 and 3. Several conclusions can be drawn based on these results:

- The content of anhydrides increases with increasing SO₃/LAB molar ratio.
- Non-sulphonated LAB decrease with increasing SO₃/LAB molar ratio.
- The content of sulphones is independent of the SO₃/LAB molar ratio.

It seems that within the tested range of SO₃/LAB molar ratios anhydrides increase more than LAB decreases, thus explaining the different slopes of the curves in Fig. 1.

After hydrolysis

As a.m. anhydrides are totally hydrolysed after hydrolysis so that only non-sulphonated LAB and sulphones are present in the free-oil. The quantitative HPLC analysis results are given in Tables 4 and 5 and are plotted in Figs. 4 and 5.

It was observed that the amount of sulphones in sulphonic acid is constant (Fig. 4) even if its proportion in free-oil

Table 4. Free-oil composition after hydrolysis (wt% in sulphonic acid)

SO ₃ /LAB	1.0	1.02	1.05	1.07	1.1
LAB	4.3	2.7	1.5	0.7	0.15
Sulphones	0.7	0.8	0.8	0.8	0.7

Table 5. Free-oil composition after hydrolysis (wt% in free-oil)

SO ₃ /LAB	1.0	1.02	1.05	1.07	1.1
LAB	86	77	64	47	17
Sulphones	14	23	36	53	83

Weight % in Sulphonic acid

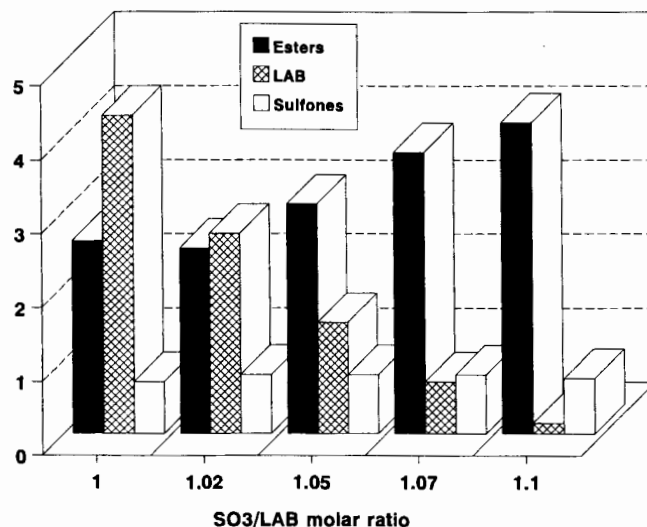


Fig. 2. Free-oil composition before hydrolysis (wt% in sulphonic acid)

Weight % in Free-oil

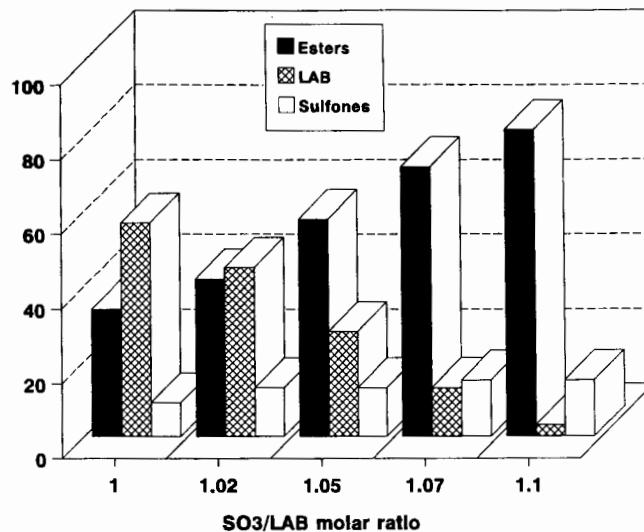


Fig. 3. Free-oil composition before hydrolysis (wt% in free-oil)

Weight % in Sulphonic acid

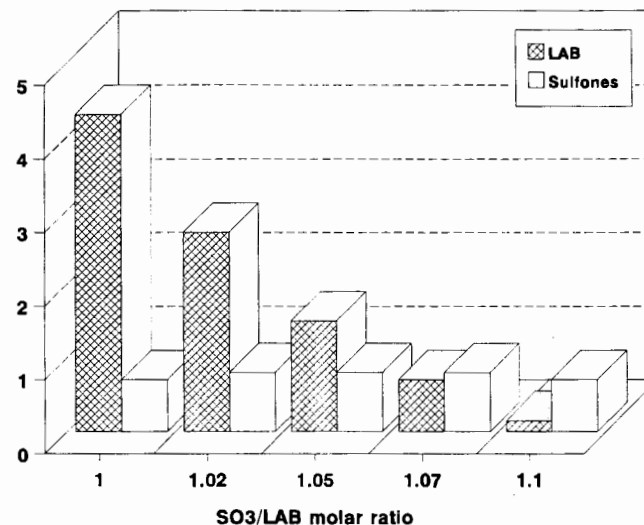


Fig. 4. Free-oil composition after hydrolysis (wt% in sulphonic acid)